High-energy Photoelectron Spectroscopy of some Antimony Compounds

By **Thomas Birchall,*** Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1
Joseph A. Connor and **Ian H. Hillier**, Department of Chemistry, University of Manchester, Manchester M13 9PL

High-energy photoelectron (p.e.) spectra have been obtained for a number of compounds of antimony. The antimony $3d(\frac{3}{2},\frac{5}{2})$ binding energies range from 542.9, 533.3 eV for $[Et_4N][SbF_6]$ to 538.6, 529.0 eV for Bu^n_3Sb, but there is little correlation with the formal oxidation state. Assignment of the oxidation state of antimony on the basis of *X*-ray p.e. data alone is not possible with certainty and even gross structural differences may remain undetected by this method.

THE binding energy of a core electron measured by high-energy photoelectron (p.e.) spectroscopy may provide an index of the formal oxidation state of the atom from which the electron originates and, as a consequence, information on the nature of the bonding in chemical compounds.[1] Recently, Tricker [2] reported *X*-ray p.e. data for some antimony(III) halide complexes and attempted to make correlations between Sb $3d$ binding energies and Mössbauer isomer shifts.[2] Two studies of the $Cs_4[Sb^{III}Sb^{V}Cl_{12}]$ system have shown that the different oxidation states of the antimony atoms in this complex can be distinguished.[3,4] We have examined a wide variety of antimony compounds by *X*-ray p.e. to test the general applicability of the findings of these previous workers and to try to obtain further information on the nature of the bonding, particularly where the $5s$ electron pair may be stereochemically inactive. We conclude that the oxidation state of antimony cannot be ascertained with certainty, neither can firm structural conclusions be drawn using this technique.

EXPERIMENTAL

The *X*-ray p.e. spectra were recorded on an A.E.I. ES-200 spectrometer using Al-K_α exciting radiation. A power level of 200 W was used throughout since higher levels caused some samples, particularly those of Sb^V, to decompose. Samples were introduced into the spectrometer by sublimation onto a copper block cooled by liquid nitrogen or, for the more involatile materials, by dusting the finely powdered material onto double-sided Scotch tape attached to the copper block of the probe. In these latter cases the probe was also cooled to liquid-nitrogen temperatures. Each spectrum was recorded several times on at least two different samples and the results averaged. Spectra of the compounds intercalated into graphite were calibrated against graphite C $1s$ 283.0 eV.[5,†] Compounds which contained no carbon, *e.g.* Sb_2O_3, $Cs_3[Sb_2X_9]$, *etc.*, were calibrated relative to C_6F_{12} (C $1s$ 292.9 eV) and/or surface hydrocarbon (C $1s$ 285.3 eV). For the remaining compounds it was found, by calibration against C_6F_{12}, that the C $1s$ binding energy for an alkyl carbon was 285.7 eV while that for an aryl carbon atom was 285.4 eV and these values were used to obtain core binding energies for the other levels. Care was taken to ensure that self-consistent results were obtained. Overlapping peaks were deconvoluted using a DuPont 310 curve resolver. All samples had been previously well characterised [6-9] or were commercial samples obtained from Alfa Inorganics. Freshly purified SbF_5 and $SbCl_5$ were intercalated into graphite by the method of Lalencette and Lafontaine [10] and were kindly provided by Mr. J. G. Ballard, McMaster University, as was the sample of SbF_4.

For each sample several levels were examined but, since the antimony $3d(\frac{3}{2},\frac{5}{2})$ levels were by far the most intense and sharpest, ranging from 1.8 to 2.3 eV in width at half height, these are, in general, the only antimony levels reported in Table 1. Within experimental error (± 0.3 eV) the doublet splitting $3d(\frac{3}{2},\frac{5}{2})$ is invariant with formal oxidation state and ligand environment. Frost *et al.*[11] made similar observations for the Co $2p(\frac{1}{2},\frac{3}{2})$ levels in cobalt compounds. At least one other level for the ligands attached to antimony is also included in this Table for each compound. Our data agree reasonably well with the few compounds that have been examined by other workers.[2]

RESULTS AND DISCUSSION

A wide variety of structural types ranging from ionic oxides, halides, and their complexes, through organoantimony oxides and halides, to simple organoantimony compounds were examined. Compounds of both the typical oxidation states (*i.e.* III and V) were examined as well as Sb_2O_4 and SbF_4 in which both oxidation states are present. The data have been arranged in order of generally decreasing Sb $3d$ binding energy but with some regard to keeping structurally related molecules together.

Binding energies (Sb $3d_{\frac{3}{2},\frac{5}{2}}$) ranged from a high of 542.9,533.3 eV for $[Et_4N][Sb^VF_6]$ to a low of 538.6,529.0 eV for Bu_3Sb^{III}, a spread of *ca.* 4 eV. Within this range the correlation of binding energy with formal oxidation state is, however, rather poor. For example, some Sb^{III}

---

† 1 eV ≈ 1.60×10^{-19} J.

[1] K. Siegbahn, C. Nordling, A. Fahlman, R. Nordberg, K. Hamrin, J. Hedman, G. Johnansson, T. Bergmark, S. E. Karlsson, I. Lindgren, and B. Lindberg, *Nova Acta Regiae Soc. Sci., Upsaliensis*, 1967, **20**, ser 4.

[2] M. J. Tricker, *Inorg. Chem.*, 1974, **13**, 742.

[3] M. J. Tricker, I. Adams, and J. M. Thomas, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 633.

[4] P. Burroughs, A. Hamnett, and A. F. Orchard, *J.C.S. Dalton*, 1974, 565.

[5] R. Nordling, H. Brecht, R. G. Albridge, A. Fahlman, and J. R. Van Wazer, *Inorg. Chem.*, 1970, **9**, 2469.

[6] T. Birchall and B. Della Valle, *Chem. Comm.*, 1970, 675.

[7] T. Birchall and B. Della Valle, *Canad. J. Chem.*, 1971, **49**, 2808.

[8] T. Birchall, P. A. W. Dean, B. Della Valle, and R. J. Gillespie, *Canad. J. Chem.*, 1973, **51**, 667.

[9] J. G. Ballard, T. Birchall, J. B. Milne, and W. D. Moffett, *Canad. J. Chem.*, 1974, **52**, 2375.

[10] J. M. Lalencette and J. Lafontaine, *J.C.S. Chem. Comm.*, 1973, 815.

[11] D. C. Frost, C. A. McDowell, and I. S. Woolsey, *Mol. Phys.*, 1974, **27**, 1473.

compounds, *e.g.* $Cs[SbF_4]$, had binding energies greater than the majority of the Sb^{V} compounds, while $Ph_3Sb^{V}S$ had almost the lowest binding energy of those examined. Measurement of the Sb $3d$ binding energy, therefore, does not seem to be a reliable indicator of oxidation state. Such a conclusion was also reached in an analogous study of tin compounds,[12] though in that case the spread of Sn $3d$ binding energies was only *ca.* 2 eV.

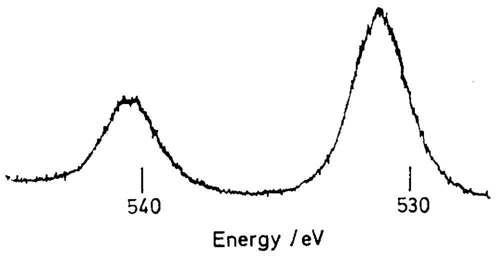
TABLE 1

Core-electron binding energies for some compounds of antimony

	Binding energy ±0.3 eV			
	Sb$3d$			
Compound	(3/2)	(5/2)		Mössbauer isomer shift in mm s^{-1} from InSb
$Na[SbF_6]$	542.2	532.6	F1s 685.6	+10.4 [8]
$[Et_4N][SbF_6]$	542.9	533.3	F1s 685.6	
SbF_5 (20% in graphite)	538.8	529.6	F1s 683.0	+10.8 [a]
(67% in graphite)	538.9	529.1	F1s 682.9	
SbF_4 Sb^{V}	542.0	532.0	F1s 685.0	+11.3 [8]
Sb^{III}	541.0	531.0		−8.3 [8]
$SbCl_5$	540.9	531.4	Cl2p 200.2	+5.44 [a]
(20% in graphite)	538.2	528.5	Cl2p 197.3	
(65% in graphite)	538.6	528.8	Cl2p 197.2	
Sb_2O_5 [b]	540.6	531.1	Sb3p 768.4, 714.6	+8.7 [6]
Sb_2O_4 [b] Sb^{V}	540.5	531.2	Sb4d 34.4	+8.9 [6]
Sb^{III}	540.0	530.7		−5.9 [6]
Sb_2O_3 [b]	539.6	530.2	Sb3p 767.7, 713.7	−3.0 [6]
Sb_2S_3	538.6	529.0	S2p 162.3	−6.0 [6]
$[Co(NH_3)_6][SbCl_6]$	540.4	530.9	Cl2p 198.9	−11.2 [c]
$[Co(NH_3)_6][Sb_2F_9]$	540.4	530.7	F1s 684.2	−6.30 [9]
$Cs_3[Sb_2Cl_9]$	539.6	530.2	Cl2p 198.9	−9.67 [9]
$[Bu^{i}H_3N][Sb_2Cl_9]$	540.5	530.8	Cl2p 199.1	−9.16 [9]
$Cs_3[Sb_2Br_9]$	540.2	530.5	Br3p 183.8, 189.5	−8.97 [9]
$Cs_3[Sb_2I_9]$	539.6	529.7	I3d 630.8, 619.0	−8.35 [9]
$Cs[Sb_2F_7]$	540.6	531.1	F1s 683.8	−4.82 [d]
$Cs_2[SbF_5]$	540.1	530.6	F1s 683.6	−4.11 [d]
$Cs[SbF_4]$	540.8	531.3	F1s 684.1	−5.02 [d]
$[Hpy][SbCl_4$	540.2	530.8	Cl2p 199.2	−8.10 [9]
$[Bu^{i}H_3N][SbI_4]$	540.2	530.5	I3d 631.2, 619.3	−7.37 [9]
$[Hpy][SbI_4]$	539.8	530.0	I3d 631.0, 619.0	
Me_3SbBr_2	540.8	531.2	Br3p 190.1, 183.2	+2.16 [e]
$(n\text{-}C_6H_9)_3SbBr_2$	540.2	530.4	Br3p 190.0, 183.1	
Ph_3SbBr_2	539.8	530.4	Br3p 189.6, 183.0	+2.24 [e]
Ph_3SbO	538.8	529.4	O1s 531.0	
Ph_3SbS	538.4	529.3	S2p 165.0	
Ph_3Sb	538.6	529.5	Sb4d 34.8	−0.61 [f]
$Bu^{n}{}_3Sb$	538.6	529.0		

[a] J. G. Stevens and L. H. Bowen, 'Mössbauer Methodology,' Plenum Press, New York, 1969, vol. 5, p. 27. [b] The O1s line was not resolved from the Sb$3d(\frac{5}{2})$ line. [c] T. Birchall, B. Della Valle, E. Martineau, and J. B. Milne, *J. Chem. Soc.* (*A*), 1971, 1855. [d] For the potassium salts. [e] J. N. R. Ruddick, J. R. Sams, and J. C. Scott, *Inorg. Chem.*, 1974, **13**, 1503. [f] T. B. Brill, G. E. Parris, G. G. Long, and L. H. Bowen, *Inorg. Chem.*, 1973, **12**, 1888.

Two studies of the mixed oxidation-state system $Cs_2[SbCl_6]$ have been made [2,4] and in both cases evidence for the presence of both Sb^{III} and Sb^{V} was obtained. However, only Burroughs *et al.*[4] obtained satisfactory resolution of the two antimony ionisations. The compounds Sb_2O_4 and SbF_4 are other examples of mixed oxidation state and it was of some interest to test the usefulness of X-ray p.e. in resolving the $3d$ bands arising from the Sb^{III} and Sb^{V} sites in cases where their environments are quite different. For Sb_2O_4 and SbF_4, the two antimony sites were not resolved, though it is obvious from the spectrum of Sb_2O_4 (Figure) that two sites are present. Deconvolution of the spectra gave a separation of only 0.5 eV between the two sets of $3d_{\frac{3}{2},\frac{5}{2}}$ bands, much smaller than in the case of $Cs_2[SbCl_6]$ where a separation of 1.8 eV has been reported.[4] Fitting of only one set of $3d_{\frac{3}{2},\frac{5}{2}}$ bands to the Sb_2O_4 spectrum resulted in lines which were significantly broader than those found for Sb_2O_3 which contains only one antimony site. The bands to higher binding energy were assigned to Sb^{V} and those to lower binding energy to Sb^{III} after comparing the spectra with those obtained for Sb_2O_5 and Sb_2O_3 (Table 1). A similar (1.0 eV) separation was found for the Sb^{III} and Sb^{V} bands in SbF_4. In view of the findings of Burroughs *et al.*[4] that $Cs_2[SbCl_6]$ underwent photoreduction, we



High-energy p.e. spectrum of Sb_2O_4 in the $3d$ region

---

[12] P. A. Grutsch, M. V. Zeller, and T. P. Fehler, *Inorg. Chem.*, 1973, **12**, 1431.

were concerned that the poor resolution in our spectra could arise from a similar process. Repetition of the spectra with fresh samples always gave reproducible spectra which did not change on prolonged exposure to the *X*-rays, even at power levels of 450 W. Power levels of this magnitude did cause photoreduction in other samples *e.g.* Ph_3Sb. This was particularly the case where fresh sample surfaces were not continually being exposed to the *X*-ray beam. We are confident that the small difference in the chemical shift of the core p.e. signals is not due to photoreduction or poor sample preparation.

The core binding energy E_i is related to the formal atomic charge q_i by the empirical relation (1) of Gelius *et al.*[13], where A is the average repulsion between a core

$$E_i = Aq_i + V_i + l \qquad (1)$$

and valence electron on atom i, V_i the potential at atom i due to the surrounding atoms, and l is a constant determining the energy origin. The value of l does not concern us since all binding energies were measured relative to a standard substance. Possible explanations for the small separation in Sb_2O_4 and SbF_4 could lie in compensating differences in Madelung potentials or in equalisation of the charges at the two sites.

In $[H_4N]_4[Sb_2Br_{12}]$ the Sb^{III} atom is in an octahedral environment of bromines while the Sb^{V} is in a site only slightly distorted from octahedral.[14] The other mixed oxidation-state halide complexes, *e.g.* $Cs_4[Sb_2Cl_{12}]$, have structures closely related to this and it has hitherto been assumed that because the two sites are similar the potential term V_i will be the same for Sb^{III} and Sb^{V} in these complexes. In Sb_2O_4 the antimony environments are quite different with the Sb^{III} very distorted while the Sb^{V} is in a site which is closer to octahedral geometry though still distorted.[15] Clearly, in Sb_2O_4 the two antimony sites experience quite different Madelung potentials. Mössbauer data on SbF_4 [8] also indicate two quite different environments for the Sb^{III} and Sb^{V} sites and again one expects the different potentials to be reflected in the core-electron binding energies.

In an attempt to rationalise the relatively large separation for $Cs_4[Sb_2Cl_{12}]$ and the small difference found for Sb_2O_4 we calculated the Madelung potentials at the antimony sites for these and related compounds using the computer program of Piken and van Gool [16] (Table 2). Such calculated lattice potentials depend very critically on accurate crystallographic data and on the charges assigned to the atoms in the unit cell. The first restriction limits the number of compounds on which calculations can be made. The effect on the calculated potentials of the assignment of charges presents a serious difficulty in assessing the final results. For example, in $Rb_4[Sb_2Br_{12}]$ the crystal is composed of Rb^+, $[Sb^{III}Br_6]^{3-}$, and $[Sb^{V}Br_6]^{-}$ ions and the indicated charges are probably close to reality. However, assignment of charges to the antimony and bromine atoms within the complex anions is more difficult. Assuming complete ionic character in the Sb–Br bond, potentials of −45.9 and −34.8 eV were obtained, whereas when 50% ionic character was assumed the potentials reduced to −16.2 and −4.9 eV respectively. These differences in potential at the two antimony sites in this complex and in $Rb_4[Sb_2Cl_{12}]$ are an order of magnitude greater than the measured difference in the related $Cs_4[Sb_2Cl_{12}]$ reported earlier.[4] Assuming that the charges on both antimony sites have been reduced to zero, the bromines have charges of $-(\frac{1}{6})$ and $-(\frac{1}{2})$ in the $[SbBr_6]^-$ and $[SbBr_6]^{3-}$ ions respectively and the calculated potentials fall to values consistent with the measured difference in the analogous chloride. For ionic Sb_2O_4 the calculated Sb potentials are even larger (Table 2), though these can be reduced considerably by assuming more covalent character (50%) in the Sb–O bonds. However, unlike the previous case, it is not possible to have charges on both antimony sites equalised since the oxygens link both sites in a polymeric structure.[15] Though some further reduction in potentials could, no doubt, be achieved by further charge sharing, this did not seem to be a reasonable approach for this material.

TABLE 2

Estimated Madelung potentials at antimony sites

Compound	V_i/eV Sb^{V}	V_i/eV Sb^{III}
$Na[SbF_6]$	−87.8	
$Rb_4[Sb_2Cl_{12}]$	−60.1	−48.0
$Rb_4[Sb_2Br_{12}]$		
(Sb^{3+}, Sb^{5+}, Br^{1-})	−45.9	−34.8
($Sb^{\frac{3}{2}+}$, $Sb^{\frac{5}{2}+}$, $Br^{\frac{1}{2}-}$)	−16.2	−4.9
(Sb^{0}, Sb^{0}, $Br^{\frac{1}{2}-}$, $Br^{\frac{1}{6}-}$)	+0.04	−1.3
Sb_2O_4		
(Sb^{3+}, Sb^{5+}, O^{2-})	−93.4	−62.0
($Sb^{\frac{3}{2}+}$, $Sb^{\frac{5}{2}+}$, O^{-})	−30.8	−8.1
Sb_2O_3		−151.9
$Cs_3[Sb_2Cl_9]$		−36.0
$Na[SbF_4]$		−48.8
$Cs_2[SbF_5]$		−39.6
$Cs[Sb_2F_7]$		−14.3

From these crude calculations it appears that there is some charge equalisation in these mixed oxidation-state compounds and the effect of this is to reduce the importance of the lattice potential on the core-electron binding energy. At the same time, equalisation of charges means that the electron-repulsion term in the Gelius equation [13] will also be reduced. In view of the large estimated values for V_i, it seems probable that the Aq_i term will be equally large and of opposite sign in order to account for the relatively small changes in core-electron binding energy from compound to compound. It also becomes apparent that, even when two clearly resolved Sb 3*d* signals are observed for a mixed oxidation-state compound, assignment of oxidation states to these signals is no longer obvious. Control samples of closely

---

[13] U. Gelius, B. Roos, and P. Siegbahn, *Chem. Phys. Letters*, 1970, **4**, 471.

[14] S. L. Lawton and R. A. Jacobson, *Inorg. Chem.*, 1966, **5**, 743.

[15] A. C. Skapski and D. Rogers, *Proc. Chem. Soc.*, 1964, 400.

[16] A. G. Piken and W. van Gool, *J. Materials Sci.*, 1969, **4**, 95.

related molecules must also be examined before any certainty can be attached to the assignment. ^{121}Sb Mössbauer spectroscopy, on the other hand, provides clear identification of the III and V oxidation states in all the mixed oxidation-state compounds prepared to date (Table 1 and refs. 17 and 18).

Within a given series of compounds there appears to be a general trend for the Sb 3*d* binding energy to decrease as the ligand electronegativity decreases. Such a correlation has already been noted by Tricker [2] and attributed to decreasing ionicity in the Sb–X bond assuming that the term dominating the binding energy is the valence term. Correlations have also been attempted between Mössbauer isomer shifts and core-electron binding energies for other series.[3,19–21] In all these cases the changes in core binding energies were small, <1 eV, and in view of our earlier discussion on the origin of the *X*-ray p.e. shifts correlations with Mössbauer data seem premature.

X-Ray p.e. data on ClF_3 and SF_4 revealed that the ionisations for the axial and equatorial F 1*s* levels could be resolved.[22] Although these measurements were carried out on gaseous samples which gave narrower lines, we were hopeful that for solid samples we might be able to distinguish between structurally different halogens as in $[\{LPtCl_2\}_2]$ complexes.[23] Unfortunately, close examination of the F 1*s*, Cl 2*p*, Br 3*p*, and I 3*d* levels in compounds known to contain both terminal and bridging, or axial and equatorial, halogens revealed no broadening of these *X*-ray p.e. levels so that the different halogen environments could not be distinguished. Further, in an examination of the $[Sb_2X_9]^{3-}$ and $[SbX_4]^-$ systems the *X*-ray p.e. data gave no indication that the members of these series are not closely related structurally. Nothing could be further from the truth, as in both series the fluoride complex has quite a different structure to the remainder of the series. The fluorides $[Sb_2F_9]^{3-}$ and $[SbF_4]^-$ have structures in which the 5*s* electron pair is stereochemically active, but for the other members of the series this is not so.[7,9]

In molecules such as $[Co(NH_3)_6][SbCl_6]$ and $Cs_3[Sb_2X_9]$ (X = Cl, Br, or I), *X*-ray and other spectroscopic evidence implies that there is no involvement of the Sb 5*s* electrons in the bonding scheme. We were hopeful that an examination of the valence-band region of the *X*-ray p.e. spectrum might reveal features which would provide direct evidence that the 5*s* electrons are not involved to any great extent in the bonding. Unfortunately the spectra in this region were too complex to allow a satisfactory analysis.

Intercalation of SbF_5 and $SbCl_5$ into the graphite lattice provides a convenient way of examining these reactive liquids. The intercalated product is much less reactive to moisture, graphite provides a convenient reference signal, and penetration of the carbon layers by the exciting radiation is sufficient to give quite intense Sb 3*d*, F 1*s*, and Cl 2*p* bands. This appears to be a convenient method for the examination of other highly reactive chlorides and fluorides. There is a significant difference in Sb 3*d* binding energy between intercalated $SbCl_5$ and $SbCl_5$ condensed directly onto the probe. However, this is more likely to be due to differences in the lattice-potential term in the Gelius equation [13] than to structure differences in $SbCl_5$ itself.

Conclusions.—The core-electron binding energies for a number of antimony compounds have been examined. The Sb 3*d* binding energies are greater for the V than the III oxidation state, but also strongly depend on the attached ligands and structure. As a result one cannot assign oxidation states with certainty on the basis of *X*-ray p.e. data alone. Furthermore, even large structural differences cannot be detected and we conclude that *X*-ray p.e. is not a very useful tool for studying the structure and bonding in compounds of antimony.

T. B. thanks Professor W. Byers Brown and the Department of Chemistry, University of Manchester for providing the facilities which allowed this work to be carried out while on sabbatical leave, 1974—1975.

[5/270 *Received*, 10*th February*, 1975]

---

[17] J. D. Donaldson, M. J. Tricker, and B. W. Dale, *J.C.S. Dalton*, 1972, 893.

[18] A. Y. Aleksandrov, S. P. Ionov, A. M. Pritchard, and V. I. Goldanski, *Soviet Physics J.E.T.P.*, 1971, **13**, 13.

[19] M. Barber, P. Swift, D. Cunningham, and M. J. Frazer, *Chem. Comm.*, 1970, 1339.

[20] W. E. Swartz, P. H. Watts, E. R. Lippincott, J. C. Watts, and J. E. Huheey, *Inorg. Chem.*, 1972, **11**, 2632.

[21] J. Adams, J. M. Thomas, G. M. Bancroft, K. D. Butler, and M. Barber, *J.C.S. Chem. Comm.*, 1972, 751.

[22] R. W. Shaw, jun., T. X. Carroll, and T. D. Thomas, *J. Amer. Chem. Soc.*, 1973, **95**, 2033.

[23] D. T. Clark, D. B. Adams, and D. Briggs, *Chem. Comm.*, 1971, 602.